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(54) **Title of the Invention:** Epoxy resin composition

(57) Abstract

Problem

To provide an epoxy resin composition that is a highly heat-resistant, highly water-resistant matrix resin for prepreg applications and that also exhibits an excellent adhesiveness for honeycomb materials.

Solution

An epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) an imidazole compound that has a cure initiation temperature lower than that of the aforesaid aromatic amine

wherein

- the dicyclopentadiene skeleton-containing epoxy resin (a) is at least 25 weight% of the total epoxy resin weight,
- the glycidylamino-functional aromatic epoxy resin (b) is at least 30 weight% of the total epoxy resin weight,
- the sum of (a) and (b) is 55 to 85 weight% of the total epoxy resin weight, and
- the equivalents ratio between the imidazole compound and epoxy resin is imidazole/epoxy = 0.005 to 0.035.

Claim

Claim 1.

An epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) an imidazole compound that has a cure initiation temperature lower than that of the aforesaid aromatic amine

wherein

the dicyclopentadiene skeleton-containing epoxy resin (a) is at least 25 weight% of the total epoxy resin weight,
the glycidylamino-functional aromatic epoxy resin (b) is at least 30 weight% of the total epoxy resin weight,
the sum of (a) and (b) is 55 to 85 weight% of the total epoxy resin weight, and
the equivalents ratio between the imidazole compound and epoxy resin is
imidazole/epoxy = 0.005 to 0.035.

Detailed Description of the Invention

[0001]

Technical Field of the Invention

The present invention relates to an epoxy resin composition that maintains heat and water resistance, that exhibits excellent resin flow control characteristics, and that exhibits excellent adhesiveness for honeycombs. More particularly, the present invention relates to an epoxy resin composition comprising epoxy resin, curing agent, and a special imidazole compound.

[0002]

Description of the Prior Art

Epoxy resin compositions are used in a variety of fields (construction, civil engineering, aviation, electrical, and so forth) as highly heat-resistant resins. Examples of these epoxy resins and materials that use them are provided hereafter. For example, Japanese Published (Examined or Kokoku or B) Patent Application Number Hei 7-17732 (17,732/1995) describes

an improved flexibility for the matrix resin used in composite materials with carbon fiber. This is achieved by incorporating a curing agent, such as diaminoxylene, in epoxy resin comprising 10 to 90 weight% tricyclodecane ring-containing epoxy resin and 10 to 40 weight% bisphenol-type epoxy resin or novolac-type epoxy resin. Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 2-51538 (51,538/1990) describes a composite material afforded by adding large amounts of dicyandiamide and diaminodiphenyl sulfone (DDS) to epoxy resin comprising glycidylamino group-containing epoxy resin and other epoxy resin. The resulting composite material exhibits an improved resistance to interlayer separation. Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 2-14213 (14,213/1990) describes the preparation of a matrix resin for composite materials that exhibit high toughness while maintaining heat resistance. This is achieved by the addition of aromatic diamine to brominated bisphenol A glycidyl ether-type epoxy resin and bisphenol F glycidyl ether-type epoxy resin. Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 5-239317 (239,317/1993) describes a resin composition afforded by adding solid rubber and an aromatic amine-type curing agent to an epoxy resin, for example, a bisphenol type. This reference also describes prepreg obtained by impregnation with a composition for which a specific relationship obtains between the viscosity measured at a 0.02 Hz vibration frequency and the viscosity measured at a 2 Hz vibration frequency. This reference also describes an improved prepreg water resistance, which is obtained by reducing the porosity produced within the layers and between the layers of the prepreg; this is achieved by carrying out fabrication by a first impregnation with a low-viscosity resin followed by impregnation with a high-viscosity resin.

[0003]

However, when these epoxy resins are employed as resins for prepregs that are used in aircraft wherein the bonding surface of the prepreg is directly joined to the honeycomb-patterned surface of a resin honeycomb followed by curing, instances are seen in regard to the bonding between the honeycomb and a prepreg that uses the aforementioned epoxy resins in which gaps are generated in this joining surface and water resistance is absent, and/or in which the prepreg and honeycomb material undergo separation during long-term use due to inadequate bonding between the honeycomb structure and the prepreg.

[0004]

Problems to Be Solved by the Invention

In order to solve the problems identified above, an object of the present invention is to provide an epoxy resin composition that is a highly heat-resistant, highly water-resistant matrix resin for prepreg applications and that also exhibits an excellent adhesiveness for honeycomb materials.

[0005]

Means Solving the Problems

The inventors carried out extensive and intensive investigations in order to solve the problems identified above and as a result discovered that an epoxy resin composition comprising specific amounts of dicyclopentadiene skeleton-containing epoxy resin, glycidylamino-functional aromatic epoxy resin, curing agent, and a specific type of imidazole in the curable components, is an excellent composition that exhibits excellent heat resistance and water resistance when applied as a prepreg matrix resin and that also exhibits satisfactory adhesiveness for honeycombs when applied as a prepreg matrix resin. This invention was achieved based on this discovery.

[0006]

More specifically, the present invention provides an epoxy resin composition comprising

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) an imidazole compound that has a cure initiation temperature lower than that of the aforesaid aromatic amine

wherein

the dicyclopentadiene skeleton-containing epoxy resin (a) is at least 25 weight% of the total epoxy resin weight,

the glycidylamino-functional aromatic epoxy resin (b) is at least 30 weight% of the total epoxy resin weight,

the sum of (a) and (b) is 55 to 85 weight% of the total epoxy resin weight, and

the equivalents ratio between the imidazole compound and epoxy resin is imidazole/epoxy = 0.005 to 0.035.

[0007]

The present invention will be described in detail in the following. The epoxy resin composition according to the present invention comprises

- (a) dicyclopentadiene skeleton-containing epoxy resin,
- (b) glycidylamino-functional aromatic epoxy resin,
- (c) aromatic amine, and
- (d) an imidazole compound that has a cure initiation temperature lower than that of the aromatic amine (c).

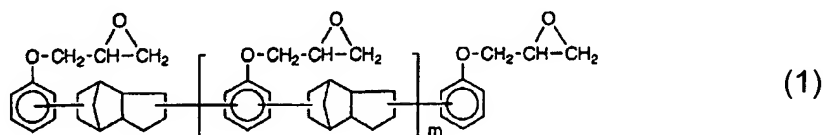
[0008]

The epoxy resin (a) used by the present invention may be any epoxy resin that contains at least one dicyclopentadiene skeleton within the molecule. A single such epoxy resin may be used, or two or more may be used in combination.

[0009]

The epoxy resin (a) can be exemplified by the tricyclo[5,2,1,0^{2,6}]decane ring-containing epoxy resin with the following structure (1) (referred to hereinbelow as the dicyclopentadiene derivative). These dicyclopentadiene skeleton-containing epoxy resins can be prepared, for example, by known methods in which dicyclopentadiene is polymerized with a cresol species (e.g., meta-cresol) or a phenol species followed by reaction with epichlorohydrin. More specifically, commercial products such as TACTIX-556 (from Dow Chemical) can be used.

[0010]



(m is an integer from 0 to 15)

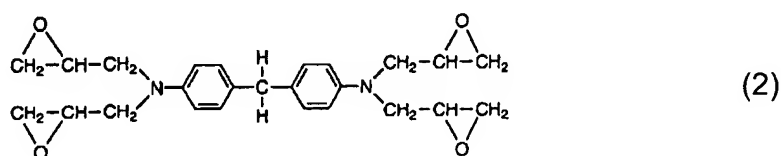
[0011]

The epoxy resin (b) used by the present invention may be any aromatic epoxy resin that contains at least one glycidylamino group within the molecule. A single such epoxy resin may be used, or two or more may be used in combination.

[0012]

This epoxy resin (b) can be exemplified by N,N,N',N'-tetraglycidyldiaminodiphenylmethane with structure (2) below, tetraglycidyl-m-xylylenediamine, triglycidyl-p-aminophenol, N,N-diglycidylaniline, and so forth. These glycidylamino-functional epoxy resins can be synthesized by known methods, for example, by the reaction of epichlorohydrin with a starting amine in the presence of a catalytic amount of water. More specifically, commercial products, such as ELM-434 from Sumitomo Chemical Co., Ltd., or TETRAD-X from Mitsubishi Gas Chemical Co., Inc., can be used.

[0013]



[0014]

The following requirements apply to the content of the epoxy resin (a) and epoxy resin (b): at least 25 weight% epoxy resin (a) with respect to the total weight of the epoxy resin; at least 30 weight% epoxy resin (b) with respect to the total weight of the epoxy resin; and (a) + (b) = 55 to 85 weight% with respect to the total weight of the epoxy resin. (a) + (b) is preferably 60 to 75 weight% from the standpoint of the viscosity controllability.

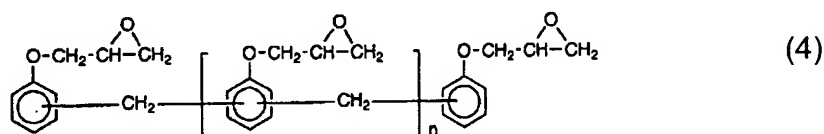
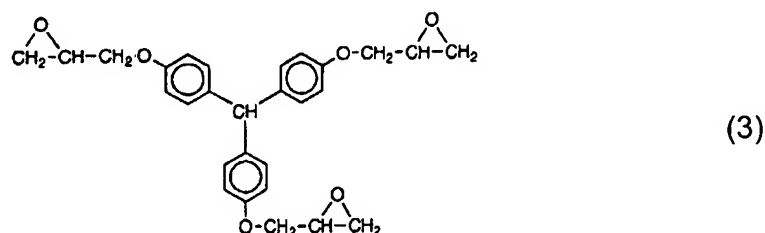
[0015]

The sum of epoxy resin (a) and epoxy resin (b) accounts for 55 to 85 weight% and preferably 60 to 75 weight% of the total epoxy resin in the epoxy resin composition according to the present invention. Values of at least 55 weight% are preferred from the standpoint of the water resistance, while values less than 85 weight% are preferred from the standpoint of the heat resistance. It is difficult to maintain the heat resistance or water resistance when the dicyclopentadiene skeleton-containing epoxy resin (a) or the glycidylamino-functional aromatic epoxy resin (b) is not present in the epoxy resin composition according to the present invention.

[0016]

In addition to the epoxy resin (a) and epoxy resin (b) that are essential components, the epoxy resin composition according to the present invention preferably contains, from the standpoint of obtaining a suitable viscosity and maintaining the heat and water resistance, 15 to 45

weight% and particularly 25 to 40 weight% of another epoxy resin (e) comprising a general-purpose epoxy resin as used in ordinary epoxy resin compositions. This additional epoxy resin (e) can be exemplified by bisphenol A-type epoxy resins, triphenylmethane-type epoxy resins, novolac-type epoxy resins, bisphenol AD-type epoxy resins, and bisphenol F-type epoxy resins. A single such epoxy resin may be used, or two or more may be used in combination. This epoxy resin can be exemplified by glycidyl ether-type epoxy resins with the following structures (3) and (4).



More specifically, commercial products, such as TACTIX-742 from Dow Chemical and EP-154 from Yuka Shell Chemical Co., Ltd., can be used.

[0017]

The aromatic amine (c) used by the present invention is an aromatic amine species that can be used as a curing agent for epoxy resins, but this aromatic amine (c) is not otherwise limited. Specific examples are diaminodiphenyl sulfone (DDS) with structure (5), infra, diaminodiphenylmethane (DDM), diaminodiphenyl ether (DPE), and bisaniline. A single such aromatic amine (c) can be used, or these can be used in mixtures of two or more. The cure initiation temperature of the aromatic amine (c) is preferably at least 150°C. An adequate heat resistance is not obtained when the aromatic amine (c) is not used.

[0018]



[0019]

While the content of the aromatic amine (c) used in the present invention is not specifically limited, the equivalents ratio with respect to the epoxy resin is, from the standpoint of generating heat resistance, preferably (active hydrogen equivalents from the aromatic amine)/epoxy equivalents = 0.6 to 1.2 and particularly 0.7 to 1.0.

[0020]

The imidazole compound (d) used in the present invention may be any imidazole that has a lower cure initiation temperature than the aromatic amine (c) used in combination with the imidazole compound in the composition according to the present invention; however, the imidazole is preferably a solid at ambient temperature. The cure initiation temperature of this imidazole (d), when measured by the rise of an exothermic peak in DSC, is preferably less than 150°C and particularly preferably is 60 to 140°C. Specific examples of this imidazole compound (d) are 2-phenyl-4-methylimidazole (2P4MZ), 2-methylimidazole (2MZ), 2,4-diamino-6-[2'-methylimidazolyl-(1)']-ethyl-s-triazine · isocyanuric acid adduct (2-MA-OK), 2-undecylimidazole (C₁₁Z), and 1-cyanoethyl-2-methylimidazole (2MZ-CN). 2-phenyl-4-methylimidazole and 2-MA-OK are preferred among the preceding from the standpoint of the separation characteristics. More specifically, commercial products, such as 2P4MZ, 2MZ, and 2MA-OK from the Shikoku Corporation, can be used.

[0021]

With regard to the proportion of the imidazole compound (d), which is a crucial point for the present invention, the imidazole compound-to-epoxy resin equivalents ratio in the epoxy resin composition according to the present invention is imidazole/epoxy = 0.005 to 0.035 and preferably 0.015 to 0.030. When this imidazole compound is monovalent, the equivalents and molar ratios are equal and the equivalents ratio is therefore given by the ratio between the molar amount of the imidazole and the total weight of the epoxy resin used/weight per epoxy group (WPE or epoxy equivalent weight). When the content of the imidazole compound (d) gives an imidazole/epoxy ratio less than 0.005, the minimum viscosity during cure will be excessively low and the composition will readily ooze out and adhesive strength for honeycomb cannot be developed. A value above 0.035 results in an excessively high viscosity that is unsuitable for prepreg fabrication.

[0022]

While the epoxy resin composition according to the present invention contains epoxy resin (a), epoxy resin (b), aromatic amine (c), and imidazole compound (d) as essential components, it

may as necessary contain, within a range that does not impair cure according to the present invention, the aforementioned additional epoxy resin (e) and various additives such as filler, ageing inhibitor, pigment, solvent, and so forth.

[0023]

The filler can be exemplified by carbon black, calcium carbonate, titanium oxide, silica, aluminum hydroxide, and so forth. The ageing inhibitor can be exemplified by hindered amines, hindered phenols, and so forth. The pigment can be exemplified by carbon black, zinc oxide, and so forth. The solvent can be exemplified by methanol, ethanol, propanol, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and so forth.

[0024]

The epoxy resin composition according to the present invention is produced by mixing the epoxy resins (a) and (b), aromatic amine (c), imidazole compound (d), and any optional additives (e.g., filler, etc.) with a paint roll or kneader and is stored in a sealed container. Depending on the application, curing is carried out by heating to about 150 to 185°C at a rate of temperature rise of about 2 to 3°C/minutes.

[0025]

During the curing step, the epoxy resin composition according to the present invention obtained as described above preferably exhibits a minimum viscosity of 10 to 1000 Poise and particularly 70 to 300 Poise, and a composition is prepared to have the actually preferred minimum viscosity.

[0026]

The resulting cured product, in addition to heat resistance and water resistance, exhibits an excellent prepreg-to-honeycomb adhesiveness, and the epoxy resin composition according to the present invention is therefore useful, inter alia, as a matrix resin composition for prepregs and as an adhesive.

[0027]

An example of the use of the inventive epoxy resin composition as the matrix resin composition for prepreg is described in the following. Prepreg according to the present invention is fabricated by impregnating the inventive epoxy resin composition into a woven fiber fabric of, for example, carbon fiber, aramid fiber (e.g., Kevlar), or glass fiber, or into these fibers laid out monodirectionally, or is fabricated by stacking a plurality of the resin-

impregnated woven fabrics. In this process, the woven fabric can be impregnated after preparing a varnish containing the inventive epoxy resin composition by dissolving the inventive epoxy resin composition in a solvent such as an alcohol (e.g., methanol, ethanol, propanol) or a ketone (e.g., methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK)). The solvent is added at 100 to 200 weight parts per 100 weight parts epoxy resin composition, wherein the drying process after fabrication is preferably optimized.

[0028]

The fiber used in prepreg according to the present invention is exemplified by woven fiber fabrics of, for example, carbon fiber, aramid fiber (e.g., Kevlar), and glass fiber, and by these fibers (long fibers) laid out monodirectionally. Specific examples here are T-300 carbon fiber from Toray Industries, Inc., and HTA Grade carbon fiber from Toho Rayon Co., Ltd. The fiber areal weight is preferably 140 to 200 g/m². Among the preceding, the prepreg is preferably fabricated by impregnating a woven fabric of carbon fiber or carbon fiber laid out monodirectionally with the aforementioned inventive epoxy resin using a solvent (e.g., varnish) or without solvent. Such prepreg can be fabricated using an apparatus such as a UD (unidirectional) machine. The content of impregnated epoxy resin composition is preferably 30 to 50 weight% in the prepreg and particularly 35 to 45 weight% in the prepreg.

[0029]

Structures can be fabricated by bonding prepreg according to the present invention to a honeycomb. Such a structure exhibits an excellent heat resistance and water resistance and also exhibits excellent honeycomb/prepreg bonding, and as a result a separate adhesive between the prepreg and honeycomb need not be used. With regard to the material of the honeycomb used with the invention, honeycomb with any composition may be used as long as the honeycomb is made of a material, e.g., resin, paper, yarn, or fiber, other than metal. For example, Nomex honeycomb, as afforded by impregnating phenolic resin into Nomex, is most preferred when considering aircraft applications. Various sizes can be used for the hexagonal columns of the honeycomb structure of the honeycomb; however, values of 1/8- to 3/8-inch for the length of the honeycomb cell size are preferred from the standpoints of weight reduction and strength.

[0030]

In addition, when prepreg has been produced using a composition according to the present invention, curing of the prepreg itself can be carried out simultaneously with bonding to the honeycomb, that is, so-called co-cure fabrication can be carried out. Figures 1 and 2 show

examples of structures in which a prepreg has been bonded to a honeycomb and describe a procedure for bonding prepreg to honeycomb. Figure 1 is an oblique drawing of a structure **1**. Figure 2 is a cross-sectional drawing in which the structure **1** has been sectioned in parallel to the sides of the polygons in a honeycomb **11**. The **a** section in Figure 2 shows a prior-art structure, while the **b** section shows a structure that uses epoxy resin composition according to the present invention. As shown in Figure 1, structure **1** is obtained by bonding a prepreg **10** to a honeycomb **11**, wherein the prepreg **10** impregnated with composition according to the present invention is mated to the end surface at one or both ends **12** of the honeycomb-structured honeycomb and fabrication is effected by heating and curing in, for example, an autoclave, while compressing from both ends.

[0031]

However, during heating and curing — and even when a uniform compression is applied to the prepreg **10** —, in some instances, as shown for the **a** section in Figure 2, the epoxy resin composition drips completely down to the lower surface **13'** while at the upper surface **13** a fillet is not formed and/or gaps are produced in sections of the prepreg **10**/honeycomb **11** bonding plane. In contrast to this, and as shown in the **b** section in Figure 2, during the cure of a structure **1** in accordance with the present invention, cure between the epoxy resin and imidazole (lower curing temperature) begins first, thereby holding the minimum viscosity of the composition steady, while cure between the aromatic amine and epoxy resin initiates at a higher temperature than the epoxy resin/imidazole cure, resulting in strong prepreg/honeycomb bonding. As a consequence of this, the inventive composition fills the gaps that have heretofore been produced between the honeycomb and prepreg by prior-art prepreg/honeycomb bonding and also avoids excessive outflow of the epoxy resin composition from the prepreg and eliminates the loss of resin component from the prepreg, thereby making it possible for the epoxy resin composition to be present in the prepreg in appropriate amounts. Accordingly, when the curing phase is begun, the viscosity of the epoxy resin composition impregnated in the prepreg **10** undergoes a temporary decline and a portion of the composition flows out onto the honeycomb **11**, thereby forming the fillet **14**. However, the composition does not undergo excessive outflow from the prepreg **10**, and curing can be completed while maintaining the shape of the fillet **14**. When, at the lower surface, the viscosity also undergoes a temporary drop, the fillet **14'** is formed due to surface tension and curing can be completed with the composition being retained to a suitable degree. This fillet is the protruding fusiform feature formed when, during prepreg/honeycomb joining and cure, a portion of the resin layer formed between the prepreg and honeycomb comes to overlie the side surface of the hexagonal column of the honeycomb (**14** and **14'** in Figure 2).

[0032]

Since the obtained viscosity control is good enough to enable co-curing for the cured product from the epoxy resin composition according to the present invention, a structure according to the present invention does not suffer from a loss of the heat resistance of the epoxy resin, has an excellent water resistance that is better than in the prior art, and exhibits excellent prepreg/honeycomb bonding. With regard to the bonding of two members such as, for example, a honeycomb and a prepreg, wherein ordinarily curing is induced in the matrix resin of the prepreg and bonding is effected using, for example, an adhesive, co-curing refers to the ability of the resin to effect bonding with the honeycomb while also being utilized as the matrix resin of the prepreg, such that cure of the matrix resin of the prepreg can be carried out simultaneously with prepreg/honeycomb bonding and without adhesive.

[0033]

The following procedure, for example, is preferred with respect to the curing conditions during honeycomb/prepreg bonding: temperature ramp up at 2-5°C/minute to 150-185°C at a pressure of 2.5-4.0 kg/cm²; holding for 1-2 hours at 150-185°C; cool down to room temperature at 2-5°C/minute. The resulting prepreg/honeycomb structure has an excellent heat resistance and water resistance and also exhibits satisfactory prepreg/honeycomb bonding, and for these reasons is useful as a member in, for example, aircraft and automobiles.

[0034]

Examples

The present invention is described in specific detail hereinbelow through examples, but the invention is not limited to these examples.

[0035]

Examples 1 to 6 [sic] and Comparative Examples 1 to 4

(i) The epoxy resin compositions

The individual epoxy resin compositions were prepared by thoroughly mixing the constituent components in the proportions reported in Table 1 below; a paint roll was also used in some cases.

[0036]

(ii) Evaluations

Each of the epoxy resin compositions prepared in accordance with (i) was subjected to the following evaluations; the results are reported in Table 1 below.

[0037]

(1) Viscosity

The minimum viscosity during composition cure was measured for each composition using a dynamic mechanical analyzer (DMA) in the parallel plate configuration (diameter = 50 mm) at a rate of temperature rise of 2°C/minute and a frequency of 10 rad/second. A curve obtained in this manner is reported in Figure 3.

[0038]

(2) Glass-transition temperature (T_g)

Using the same conditions as for honeycomb/prepreg bonding, cured product was prepared from each composition by raising the temperature at 2°C/minute and curing for 2 hours at 180°C. A 5 × 5 × 15 mm bar was cut from the cured product and was submitted to measurement with a thermomechanical analyzer (TMA) using a penetration procedure at a rate of temperature rise of 10°C/minute and a load of 100 g. A graph was prepared from the results, and the midpoint of the inflection point is reported as T_g .

[0039]

(3) Glass-transition temperature (T_g) after water resistance testing

Cured product was prepared as in (2) by curing for 2 hours at 180°C and was immersed for 14 days in hot water (93°C). Upon withdrawal, the sample was immediately submitted to measurement of the glass-transition temperature (T_g) by TMA using a penetration procedure (measurement conditions as above).

[0040]

(4) Prepreg moldability

A carbon prepreg was fabricated by impregnating 38% of a composition as reported in Table 1 into carbon fiber (T-300 from Toray Industries, Inc., fiber areal weight = 190 g/m²) using a UD machine from The Yokoyama Rubber Co., Ltd. A score of "O" was rendered when the composition gave no problems with flow and impregnation characteristics at the machine; a score of "x" was rendered when the viscosity was high and impregnation could not be carried out.

[0041]

(5) Fillet formability

Prepreg fabricated in accordance with (4) was mated onto Nomex honeycomb (Showa Aircraft Industry Co., Ltd.) on both of the surfaces that presented the honeycomb pattern. The temperature was raised to 180°C at a rate of temperature rise of 2°C/minute in an autoclave while applying a pressure of 3 kg/cm² and this temperature was then held for 120 minutes. The resulting sample was sectioned in parallel to the polygonal columns of the honeycomb: a score of "O" was rendered when a fillet was formed at both the upper and lower ends of the honeycomb; a score of "x" was rendered either when a fillet was not formed or when there was a fillet only on the lower surface. The results are reported in Table 1 below.

[0042]

Table 1.

CIT = cure initiation temperature

| | Ex. 1 | Ex. 2 | Ex. 3 | Ex. 4 | Ex. 5 | Ex. 6 | Ex. 7 | Comp. Ex. 1 | Comp. Ex. 2 | Comp. Ex. 3 | Comp. Ex. 4 |
|---|-------|-------|-------|-------|-------|-------|-------|----------------|----------------|----------------|----------------|
| (b) glycidylamine type ELM-434 | 50 | 50 | 50 | 50 | 50 | 45 | 55 | 50 | 50 | 25 | 75 |
| (a) dicyclopentadiene type TACTIX-556 | 25 | 25 | 25 | 25 | 25 | 30 | 27 | 25 | 25 | 20 | 20 |
| (e) other epoxy TACTIX-742 | 20 | 20 | 20 | 20 | 20 | 20 | 15 | 20 | 20 | 50 | |
| EP-154 | 5 | 5 | 5 | 5 | 5 | 5 | 3 | 5 | 5 | 5 | 5 |
| epoxy equivalent weight | 147 | 147 | 147 | 147 | 147 | 152 | 146 | 147 | 147 | 157 | 129 |
| DDS (CIT = 166°C) | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 | 31 |
| type of imidazole (CIT) | | | | | | | | | | | |
| 2P4MZ (120°C) | 0.5 | 2.0 | 3.0 | 1.0 | | 2.0 | | 0.1 | 5.0 | 2.0 | 2.0 |
| 2MZ (63°C) | | | | | 3.0 | | 1.5 | | | | |
| 2MA-OK (130°C) | | | | | 0.012 | 0.021 | 0.027 | | | | |
| imidazole/epoxy | 0.005 | 0.020 | 0.028 | 0.018 | 0.012 | 0.021 | 0.027 | 0.002 | 0.046 | 0.02 | 0.016 |
| Tg | 205 | 205 | 207 | 208 | 207 | 200 | 205 | 201 | 200 | 202 | 168 |
| Tg after water resistance testing | 190 | 192 | 193 | 193 | 190 | 188 | 192 | 189 | 189 | 172 | 155 |
| minimum viscosity (Poise) of the resin composition | 20 | 30 | 600 | 100 | 20 | 55 | 120 | 5 | 9000 | 85 | 7 |
| prepreg moldability | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | × | ○ | ○ |
| fillet formability | ○ | ○ | ○ | ○ | ○ | ○ | ○ | × | × | ○ | × |

[0043]

Notes to the Table.

The amount of each component is reported in weight parts.

ELM-434: glycidylamine-type epoxy resin with formula (2), supra, from Sumitomo Chemical (epoxy equivalent weight = 120)

TACTIX-556: dicyclopentadiene-type epoxy resin with formula (2) [sic], supra, from Dow Chemical (epoxy equivalent weight = 230)

TACTIX-742: triphenylmethane triglycidyl ether (epoxy equivalent weight = 160) from Dow Chemical

EP-154: phenol novolac-type epoxy resin (epoxy equivalent weight = 180) from Yuka Shell Chemical

DDS: 4,4'-diaminodiphenyl sulfone from Sumitomo Chemical, cure initiation temperature = 166°C

2P4MZ: 2-phenyl-4-methylimidazole from Shikoku Corporation, cure initiation temperature = 120°C

2MZ: 2-methylimidazole from Shikoku Corporation, cure initiation temperature = 63°C

2MA-OK: 2,4-diamino-6-[2'-methylimidazolyl-(1)']-ethyl-s-triazine · isocyanuric acid adduct from Shikoku Corporation, cure initiation temperature = 130°C

[0044]

Figure 4 contains a graph of the relationship between the minimum viscosity during composition cure and the imidazole/epoxy equivalents ratio for the individual imidazoles during cure of the compositions prepared in the individual examples and comparative examples. It is shown that the epoxy resin composition according to the present invention, when used as a prepreg, exhibits an optimal minimum viscosity when the imidazole/epoxy equivalents ratio is in the range of 0.005 to 0.035.

[0045]

Advantageous Effects of the Invention

The epoxy resin composition according to the present invention, while maintaining heat resistance and water resistance, provides excellent prepreg/honeycomb bonding, and, when used as the matrix resin in a prepreg, can be controlled to a viscosity that provides a good-quality fillet with a honeycomb. As a consequence, the epoxy resin composition according to the present invention is useful in particular as a matrix resin composition for prepreg that is to be bonded to a resin honeycomb. The epoxy resin composition according to the present

invention exhibits a viscosity controllability that makes it possible for the prepreg to exhibit curability.

Brief Description of the Drawings

Figure 1 is an oblique drawing of a structure comprising a honeycomb and prepreg.

Figure 2 is a cross-sectional diagram of a structure comprising a honeycomb and prepreg.

Figure 3 is a graph of the relationship between temperature and viscosity during the cure of an epoxy resin composition.

Figure 4 is a graph of the relationship, for data from the examples and comparative examples, between the imidazole compound/epoxy resin equivalents ratio and the minimum viscosity of the composition during cure.

Reference Symbols

| | | |
|-----|-------|--|
| 1 | | structure |
| 10 | | prepreg |
| 11 | | honeycomb |
| 12 | | end |
| 13 | | upper surface |
| 13' | | lower surface |
| 14 | | upper fillet |
| 14' | | lower fillet |
| a | | prior-art structure |
| b | | structure according to the present invention |
| c | | cell size |

Figure 1.

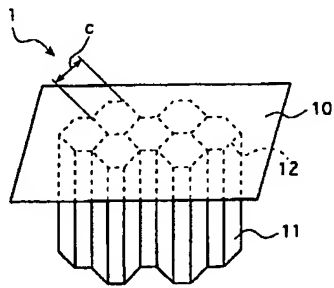


Figure 2.

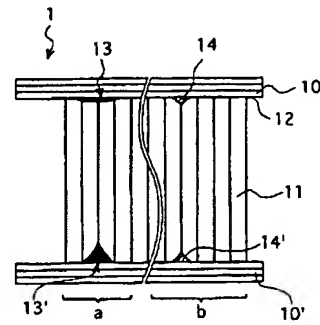


Figure 3.

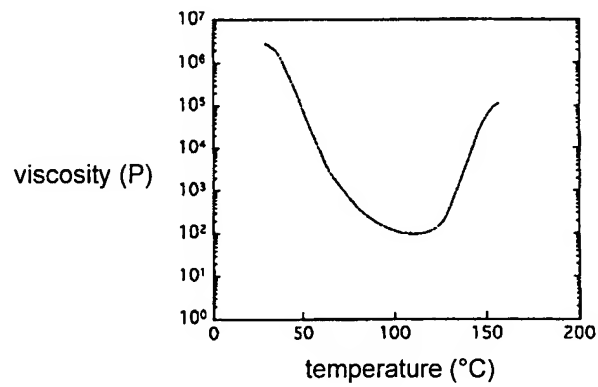


Figure 4.

